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TOXIC ORGANIC VOLATILIZATION
FROM LAND TREATMENT SYSTEMS

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ABSTRACT

Methodology was evaluated for estimating volatilization of toxic organic chemicals from unsaturated soils. Projections were compared with laboratory data for simulated rapid infiltration wastewater treatment systems receiving primary municipal wastewater spiked with a suite of 18 toxic organic compounds, nine of which were considered volatile. Predictions within a factor of 2 were possible under the quasi-steady state conditions of the experiment for most compounds applied. Volatilization was calculated by applying Fick's second law under the experimental conditions.

Index words: 1,1-dichloroethane, trichloroethene, 1,1,2,2-tetrachloroethene, chloroform, 1,1,1-trichloroethane, toluene, dibromochloropropane, 2-chloroethylvinyl ether, chlorobenzene, wastewater

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INTRODUCTION

The commercial production of organic compounds has increased steadily during the last forty years. Land treatment and disposal of these chemicals is resulting in the potential transport of toxic chemicals to groundwater. Nevertheless, this problem has been largely ignored principally because of the conception that the natural processes in the soil have an enormous capacity to degrade organic compounds and because of difficulties in trace organic analysis. Recent improvements in analytical methodology for organic pollutants have resulted in observations of widespread pollution of groundwater by organic chemicals.

Preservation of the quality of our valuable and irreplaceable soil and groundwater resources requires control of the releases of organic chemicals into the soil mantle. To establish control measures that adequately protect our resources yet permit reasonable utilization of the soil as a treatment system, models are needed that describe the transport and fate of the chemicals in soil systems. This investigation was designed to evaluate a methodology for predicting transport and fate of organic chemicals in land treatment systems and demonstrate with selected laboratory data the suitability of the methods for estimating volatilization of organic chemicals from the unsaturated soil of a simulated rapid infiltration system.

METHODS AND MATERIALS

Soil from the Lincoln series, a mixed thermic typic ustifluvent, was collected in 10 cm increments from a profile near Ada, Oklahoma (see Table 1). Columns of borosilicate glass process pipe, 15 cm ID X 150 cm with blown sampling ports at 7 1/2, 15, 30, and 60 cm, were packed with soil to a bulk density (ρ) of 1.6 g/cm³. Each 10 cm increment was packed in the same relative position occupied in the original profile. The saturated hydraulic conductivity of the seven packed columns was 3.47 ± 0.29 cm/hr. The average soil pore water content ($\theta = 0.21$) was determined from the retention volume of a slug of tritiated water. To protect the biota, the soil was not dried or sieved, and the columns were packed soon after collection of the soil. To permit evaluation of volatilization, the top of each column was enclosed in a "greenhouse" 45 cm in height also of borosilicate process pipe. Using a vacuum source, room air was flushed through the greenhouse at 2 l/sec.

The experimental configuration is shown in Figure 1. Unless otherwise noted, all materials that contacted the feed solution, soil, or effluents were either borosilicate glass or Teflon. To minimize volatilization loss of organic compounds added to the wastewater, the organic feed solution was stored inside Teflon gas sampling bags with a Teflon septum valve (Alltech Assoc, Arlington Heights, IL). The bag was fitted inside a sealed glass container filled with water. Water was pumped into the container around the bag with a peristaltic metering pump, which forced the feed solution from the bag into a mixing chamber.

Primary wastewater (Table 1), collected fresh daily, was stored in a refrigerator at 4°C and pumped using a peristaltic pump with a short section of silicone pump tubing to a mixing chamber. After combination in

the mixing chamber, the combined flows were delivered to the soil column using a siphon. Compressed air at 14 KPa was used to start the siphon action. It was necessary to provide a vent in the head space of the mixing chamber to permit operation of the siphon.

Three columns received primary municipal wastewater amended with a suite of organic chemicals (see Table 2). Three received just primary municipal wastewater and one received groundwater and the suite of organic chemicals. The columns received 4.40 ± 0.17 cm of feed solution each day. This was accomplished by dosing the columns with equal quantities of feed every four hours. Timing control utilized the crystal clock of a microprocessor. The actual composition of the water applied to the soil was monitored throughout the experiment for the compounds shown in Table 2, but the discussion will be limited to the volatile compounds.

SAMPLING AND ANALYTICAL PROCEDURES

Sampling and analysis of the solutions associated with the column study were divided into six compartments. The analyses associated with each compartment are summarized in Table 3. Analysis of both the old and the fresh dosing solutions was performed twice weekly, coincident with the preparation of fresh solution. Primary sewage, dosed primary, and column effluents were analyzed at approximately weekly intervals throughout the course of the study. After the composition of the column effluents had stabilized, analysis of sampling port effluents was begun with the functioning ports from each column sampled once every two weeks. The head space above the dosed columns was sampled several times to obtain information on the degree of volatilization.

Column Dosing

Two dosing cocktails, one for volatile organics and one for extractables, were prepared by combining pure compounds (by mass) in a reaction vial. To prepare the dosing solution that ultimately fed the columns, syringe-measured aliquots of each cocktail were added aseptically to two liters of filter sterilized spring water. The flask was stoppered to exclude air and the zero head space mixture was magnetically stirred for 48-72 hours before use. The 1:15 dilution of the dosing solution administered to the columns produced a nominal influent concentration of 500 µg/liter as carbon of each component.

Precautions were taken to achieve and maintain sterility in the dosing system. All glassware and Teflon contacting the dosing solution were autoclaved weekly. The preparation flask and stopper were fired at 550°C. The spring water was pressure filtered through 0.45 µm and, later in the study, 0.2 µm pore size membranes. All solutions were transferred

using pressure from bottled breathing quality air.

Sampling

Primary sewage was grab sampled directly from the refrigerated storage reservoir. Dosed primary was collected by uncoupling the tubing below the mixing chamber and allowing the dosed solution to drain directly into collection vessels. Column effluents were collected by gravity flow in iced Erlenmeyer flasks. Column sampling port effluents were drawn by applying a light vacuum to the collection system and Tenax traps were used to capture volatilized compounds. Column head space was sampled by drawing a measured portion of the air removed from the head space through a Tenax trap. The air was sampled for a 24 hour time period.

Analysis

All analyses for volatile organics were performed on a Hewlett Packard (HP) Model 5880 Gas Chromatographic System equipped with an HP Model 7575A Purge and Trap Sampler. Dosing solutions, primary sewage, dosed primary, and column and port effluent samples were run by conventional solution purge and trap techniques on a 2 mm x 1.9 m glass column packed with 0.2% Carbowax 1500 on 80/100 mesh Carbopack-C and using two internal standards. Samples collected on Tenax traps were inserted into the instrument and purged in the same manner as the other samples.

Quality Assurance

Quality assurance procedures were designed to evaluate the variance associated with the analytical determinations employed and, in the organic analyses, the variance associated with sample preparation. Quality control precautions were generally in accord with U.S. EPA (1972).

Water from Byrd's Mill Spring (BMSW), the local ground water supply, was used for the preparation of all organic solutions because it consistently gave a cleaner GC blank than the purified house water. The deionized distilled house water was used for inorganic standards and for cleaning glassware. All glassware used in organic analysis was fired in an annealing oven (maximum temperature of 550°C) to eliminate contamination. Standards and dosing solutions were prepared with research grade chemicals and solvents, all of which were evaluated by GC analysis of stocks and blanks.

Purge efficiencies were determined on standard solutions of each of the volatile organics. Analytical replicates were run on 25 percent of the volatile organic samples. The internal standard method of quantitation was used for all GC organic analyses. Spike component peaks were generally unambiguously identified in the chromatogram by retention times. In cases where doubt arose, GC-MS was used to verify the presence of the compounds in question. Relative response factors, with frequent calibration runs (at least daily), were closely monitored to insure quality in the quantification of the GC results.

RESULTS AND DISCUSSION

Due to the operation of the system the highest chemical concentration at "quasi steady-state" should be at or near the surface of the soil. The approximation is based on a steady-state solution to a transient situation where the cyclic operation of the columns and the depth of water applied for each cycle is known.

For conservation of mass, the mass flux of chemical applied at the surface should be equal to the total flux due to vapor transfer plus liquid transfer out of a surface zone. The solution was developed assuming no degradation. Vapor flux according to Fick's second law can be written:

$$J_v = D_s \frac{\partial C_v}{\partial x} \quad (1)$$

where:

J_v = flux of vapor

D_s = effective diffusion coefficient ($\text{cm}^2 \text{sec}^{-1}$)

C_v = concentration in vapor phase (mg l^{-1}) x distance along flow path.

Millington and Quirk (1961) related diffusion in air filled pores to the air filled porosity (η) and the total porosity (P_T) to account for the tortuosity of the pores on vapor transport using the equation:

$$D_s = D_o \left(\frac{\eta^{10/3}}{P_T^2} \right) \quad (2)$$

where D_o = diffusion coefficient of the chemical in air. For the columns under consideration where $\theta = 0.21$, $\rho = 1.6 \text{ g/cm}^3$, and the soil particle density is assumed to be 2.65, the total porosity is 0.4 and

$$D_s = 0.025 D_o \quad (3)$$

The diffusion coefficient for toluene is $0.071 \text{ cm}^2 \text{sec}^{-1}$ at 273°K (Boynton and Brattain, 1929) and the temperature relationship is

$$D_{oT} = 0.071 \left(\frac{T}{273} \right)^{1.75} \quad (4)$$

Each application of water was 0.73 cm and would replace 3.5 cm of soil solution if the water content remained a constant 0.21. For this reason, it will be assumed the maximum concentration for each of the compounds will occur at 3.5 cm and remains constant at that depth. The total vapor loss is assumed to be upward and restricted by the surface 3.5 cm soil layer since the downward concentration gradient of quasi steady-state will be small if any (Table 5).

The concentration in the vapor phase was estimated based on the work of Dilling (1977) where the liquid-vapor partition coefficient (K) is given by the equation

$$K = \frac{T S}{16.04 PM} \quad (5)$$

where:

P = vapor pressure of the pure solute (mm Hg)

M = gram molecular weight of the compound

T = temperature ($^{\circ}\text{K}$)

S = solubility of solute in water (mg l^{-1})

Liquid-vapor partition coefficients, molecular weight and solubility are tabulated in Table 4 for the compounds considered in this study.

The vapor flux in $\mu\text{g cm}^{-2} \text{ hr}^{-1}$ can then be calculated as

$$J_v = \frac{2}{K} C_{3.5} \quad (6)$$

where $C_{3.5}$ refers to the liquid phase concentration in mg l^{-1} at 3.5 cm.

The liquid flux ($\mu\text{g cm}^{-2} \text{ hr}^{-1}$) leaving the 3.5 cm depth at steady-state is

$$J_L = V_d C_{3.5} \quad (7)$$

where V_d is the darcy flux (cm hr^{-1}), not the interstitial velocity. The conservation of mass equation then is

$$0.18C_0 = 0.18 C_{3.5} + \frac{2}{K} C_{3.5} \quad (8)$$

where C_0 = applied liquid phase concentration (mg l^{-1}). The results from Equation 8 are tabulated in Table 5 along with the applied concentration, predicted amount volatilized, and measured amount volatilized.

The prediction of the amount volatilized was within a factor of two of the measured results. Considering the standard deviation in the measurements these estimates appear to reflect the observations. Three exceptions occurred. For toluene and 2-chloroethylvinyl ether, the observations were significantly less than predicted. This may be due to rapid degradation. Measured data from the sampling ports for 2-chloroethylvinyl ether show a continued decay in the observed concentration while the decay in toluene may be too rapid to be readily measured under these experimental conditions. Dibromochloropropane appeared to volatilize more than predicted; this may be due to uncertainty in vapor pressure or water solubility in the form applied.

Although the research described in this article has been funded wholly or in part by the United States Environmental Protection Agency through inhouse research, it has not been subjected to the Agency's required peer and policy review and therefore does not necessarily reflect the views of the Agency and no official endorsement should be inferred.

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TABLE 1. SOIL AND APPLIED WASTEWATER PROPERTIES

	Mean [†]	Range*
pH	6.4	6.6 - 6.1
CEC meg/100g	3.5	4.8 - 2.3
Sand %	92	95 - 89
Silt %	5.9	8.0 - 4.0
Clay %	2.1	3.5 - 1.5
Organic Carbon %	0.087	0.22 - 0.02
Bulk Density g/cm ³	1.6	
Water Content	0.21	
Air filled porosity	0.19	
Hydraulic Conductivity cm/hr	3.47	
TOC mg/l	55 ^{††}	
Total N mg/l	23 ^{††}	
NO ₃ mg/l	0.2 ^{††}	
Total P mg/l	7 ^{††}	

† Mean through the 150 cm profile.

* Range through the 150 cm profile.

†† Applied wastewater.

TABLE 2. COMPONENTS OF THE DOSING COCKTAILS

Volatile Cocktail Components	Extractable Cocktail Components
1,1-dichloroethane	Chlorobenzene*
Trichloroethene	1,2-dichlorobenzene
1,1,2,2-tetrachloroethane	1,2,4-trichlorobenzene
Chloroform	Nitrobenzene
1,1,1-trichloroethane	bis-(2-chloroethyl)ether
Toluene	Phenol
Dibromochloropropane	2-chlorophenol
2-chloroethylvinyl ether	2,4-dichlorophenol
Chlorobenzene*	2,4,6-trichlorophenol
	Diethyl phthalate

* Analyzed as both volatile and extractable compound.

TABLE 3. ANALYSES PERFORMED ON LARGE COLUMN STUDY COMPARTMENTS

Compartment	Volatile Organics	Extractable Organics	Inorganics
Primary Sewage	X	X	X
Dosing Solution	X	X	
Dosed Primary	X	X	
Column Effluent	X	X	X
Sampling Port Effluents	X	X	
Column Head Space	X		

TABLE 4. PROPERTIES OF VOLATILE COMPOUNDS APPLIED TO EXPERIMENTAL SYSTEM

Compound	Molecular wt (g)	Solubility in Water (mg/l) [†]	Vapor Pressure mm Hg [†]	Liquid/Vapor Partition Coef. (k) ^π
chlorobenzene	112.56	500 @ 20°C ^{††}	11.8 @ 25°C ^{††}	7.0
chloroform	119.38	7,840	192	6.35
1,1-dichloroethane	98.96	5,100	260	3.68
1,1,1-trichloroethane	133.41	720	124	0.81
trichloroethene (TCE)	131.5	1,100	74	2.1
tetrachloroethene (PCE)	165.83	150 @ 25°C ^{††}	14 @ 20°C ^{††}	1.2
toluene	92.1	515 @ 20°C ^{††}	22 @ 20°C ^{††}	4.7
2-chloroethylvinyl ether	106.35	15,000 [§]	26.75 @ 20°C [§]	93
dibromochloropropane (DBCP)	236	600 [#]	0.8 @ 20°C [*]	53

†† Verschueren (1977)

† Dilling (1977) unless noted

§ EPA 440/4-79-0296

π Calculated from Dilling (1977)

Stuart Cohen personal communication

* Joles, Z.E. 1966

TABLE 5. MEASURED AND PREDICTED CONCENTRATIONS OF VOLATILE COMPOUNDS AS A FUNCTION OF DEPTH

	1,1-dichloro-ethane	trichloro-ethene	tetrachloro-ethene	chloroform	1,1,1-trichloro-ethane	toluene	1,1,1-trichloro-ethane	2-chloroethyl-vinyl ether	chloro-benzene
	µg/liter								
Measured* Volatilized	669 ± 94	848 ± 264	408 ± 279	2810 ± 506	1436 ± 274	59.7 ± 8.7	1202 ± 155	529 ± 122	48.6 ± 3.3
Calculated* Volatilized	944	926	394	2411	1515	212	461	116	221
Measured Applied (0 cm)	1248 ± 222	1096 ± 309	436 ± 135	3752 ± 639	1623 ± 393	300 ± 50.4	2803 ± 738	1116 ± 355	355 ± 74
Calculated (3.5 cm)	304	170	42	1341	108	88	2346	1000	134
Measured Port 1 (7.5 cm)	126 ± 69	50 ± 13	26 ± 22	492 ± 180	58 ± 12	27 ± 34	1452 ± 670	260 ± 58	3.5 ± 3.6

* To facilitate observation of the concentration of mass, values reported are the concentration that would have been achieved if the quality of material that volatilized was dissolved in a volume of water equal to the volume of applied solution. (Absolute quantity recovered/volume of feed applied over the sampling interval).

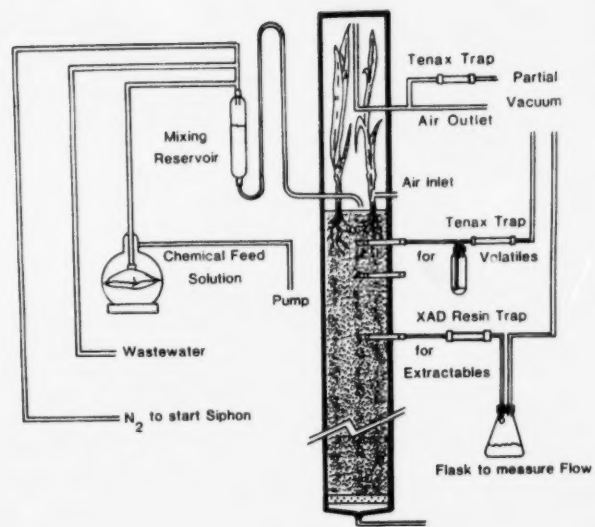


FIGURE 1. Experimental Configuration